

MANGANESE COMPOUNDS

Manganese compounds are federal hazardous air pollutants and were identified as toxic air contaminants in April 1993 under AB 2728.

CAS Registry Number: Manganese 7439-96-5

Mn

Molecular Formula: Mn

Manganese is an odorless, silvery, white, lustrous, hard, brittle metal. It exists in four allotropic forms and readily dissolves in dilute mineral acids and in aqueous solutions of sodium or potassium bicarbonate. Manganese is superficially oxidized on exposure to air, and burns with an intense white light. When heated, it reacts with carbon, phosphorus, antimony, or arsenic (Merck, 1989). Manganese dust or powder is flammable (Sax, 1987). Manganese colors glass an amethyst color and is responsible for the color of true amethyst (HSDB, 1991).

Examples of Manganese Compounds

manganese acetate	manganese fluoride
manganese acetylacetonate	manganese methylcyclopentadienyl
manganese chloride	manganese oxide trifluoride
manganese cyclopentadienyl	manganese perchlorate
manganese dimethyl	manganese sulfate
manganese dioxide	manganese sulfide
manganese dithiocarbamate telluride	manganese tetrahydroaluminate
manganese ethylenebis(dithiocarbamate)	manganese tricarbonyl fluoride

Physical Properties of Manganese

Synonyms: colloidal manganese; cutaval

Valences:	2,4,7 (common) 1,3,5,6 (rare)
Molecular Weight:	54.938
Boiling Point:	1,962 °C
Melting Point:	1,244 °C
Density/Specific Gravity:	7.47 at 20 °C (alpha) (water = 1)
Vapor Pressure:	1 mm Hg at 1,292 °C

(Merck, 1989; Sax, 1989; U.S. EPA, 1994a)

SOURCES AND EMISSIONS

A. Sources

Manganese is used for rock crushers, railway points and crossings, wagon buffers, ceramics, matches, glass, dyes, welding rods, steel alloys, cast iron, and alloys (HSDB, 1991). It also is used in dry cell batteries, glass, inks, paints, rubber and wood preservatives, and fungicides.

Mancozeb (manganese ethylene bis dithiocarbamate, zinc salt) is registered as a fungicide. It is used for the prevention and control of agricultural plant diseases on a variety of fruit, vegetable, and fiber (cotton) crops. It is also registered for use as a seed treatment (DPR, 1996).

Maneb (manganese ethylene bis [dithiocarbamate]) is registered as a fungicide. It is used for the prevention and control of agricultural plant diseases on a variety of fruit, vegetable, and fiber (cotton) crops. It is also registered for disease prevention and control in nurseries for application to ornamental grasses, flowers, shrubs, and trees (DPR, 1996).

Manganese sulfate is registered as an adjuvant/nutrient. It is used on a variety of fruit (citrus, stone, and pome fruit), and leafy and fruiting vegetables. The licensing and regulation of pesticides for sale and use in California are the responsibility of the Department of Pesticide Regulation (DPR). Information presented in this fact sheet regarding the permitted pesticidal uses of mancozeb, maneb, and manganese sulfate has been collected from pesticide labels registered for use in California and from DPR's pesticide databases. This information reflects pesticide use and permitted uses in California as of October 15, 1996. For further information regarding the pesticidal uses of these compounds, please contact the Pesticide Registration Branch of DPR (DPR, 1996).

The primary stationary sources that have reported emissions of manganese compounds in California are ship-building and repair facilities, petroleum refining, and electrical services (ARB, 1997b). Manganese has also been identified in motor vehicle exhaust by the Air Resources Board (ARB) (ARB, 1991e).

B. Emissions

The total emissions of manganese from stationary sources in California are estimated to be at least 130,000 pounds per year and manganese compounds to be at least 1,700 pounds per year, based on data reported under the Air Toxics "Hot Spots" Program (AB 2588) (ARB, 1997b).

C. Natural Occurrence

Manganese constitutes 0.085 percent of the earth's crust. It occurs in ores such as rhodochrosite; pyrolusite; hausmannite; manganite; manganosite; braunite; and psilomelane and in minute amounts in plants, animals, and water (HSDB, 1991).

AMBIENT CONCENTRATIONS

Manganese is routinely monitored at the statewide ARB air toxics network. The network's mean concentration of manganese from January 1996 through December 1996 is estimated to be 21.2 nanograms per cubic meter (ng/m^3) (ARB, 1997c). The United States Environmental Protection Agency (U.S. EPA) also compiled ambient concentration data from several study areas throughout the United States from 1980-91. Information from these studies reports a mean of approximately 11 ng/m^3 (U.S. EPA, 1993a).

At the request of the DPR, the ARB conducted a four-week ambient air monitoring program in populated areas near expected applications of mancozeb in Kern County in spring of 1993. In addition, three-day monitoring was conducted during and after an aerial application to a potato field in the same county and time period. The monitoring was coordinated to collect samples during the month of peak use in the county of peak use. Of the more than 50 samples collected during the four-week program, none were found to be above the minimum detection limit of 0.5 micrograms per sample (ARB, 1994c). Results for those samples collected around the potato field were concentrations ranging from not detected to 1.81 micrograms per cubic meter ($\mu\text{g}/\text{m}^3$), with the maximum value measured during the application (ARB, 1994d).

INDOOR SOURCES AND CONCENTRATIONS

Major sources of indoor airborne manganese identified by source apportionment include infiltration of outdoor air, smoking, cooking, ultrasonic humidifiers, and other indoor sources (Ozkaynak et al., 1996; Lewis, 1991). The "other" indoor sources were unidentified, but may have included activities such as cleaning, dusting, vacuuming, and hobbies.

Manganese was measured in about 170 homes during the fall of 1990 in southern California. Indoor PM_{10} (particles less than 10 microns in diameter) concentrations of manganese ranged from 10 to 190 ng/m^3 with an average of 40 ng/m^3 during the daytime, and from 7 to 74 ng/m^3 with an average of 23 ng/m^3 during the nighttime. Outdoor manganese concentrations ranged from 26 to 230 ng/m^3 with an average of 53 ng/m^3 during the daytime, and from 17 to 100 ng/m^3 with an average of 38 ng/m^3 during the nighttime (Pellizzari et al., 1992).

Manganese concentrations (PM_{10}) measured by personal exposure samplers during the daytime were much greater than the concentrations measured indoors or outdoors at these homes. Personal exposure to manganese concentrations ranged from 19 to 390 ng/m^3 with an average of 64 ng/m^3 during the daytime, and from 8 to 72 ng/m^3 with an average of 25 ng/m^3 during the nighttime (Pellizzari et al., 1992).

In a study of public buildings in the eastern United States, 24-hour manganese concentrations in hospitals, offices, and nursing homes ranged from non-detectable to 16 ng/m^3 , much lower than outdoor levels at these buildings (Sheldon et al., 1988).

ATMOSPHERIC PERSISTENCE

Manganese compounds will exist in the particle phase in the atmosphere, and hence be subject to wet and dry deposition. The average half-life and lifetime for particles in the troposphere is estimated to be about 3.5 to 10 days and 5 to 15 days, respectively (Balkanski et al., 1993; Atkinson, 1995).

AB 2588 RISK ASSESSMENT INFORMATION

The Office of Environmental Health Hazard Assessment reviews risk assessments submitted under the Air Toxics “Hot Spots” Program. Of the risk assessments reviewed as of December 1996, for non-cancer effects, manganese and manganese compounds contributed to the total hazard index in 34 of the approximately 89 risk assessments reporting a total chronic hazard index greater than 1, and presented an individual hazard index greater than 1 in 2 of these risk assessments. Manganese and manganese compounds also contributed to the total hazard index in 1 of the approximately 107 risk assessments reporting a total acute hazard index greater than 1 (OEHHA, 1996b).

HEALTH EFFECTS

Probable routes of human exposure to manganese are inhalation and ingestion (HSDB, 1991).

Non-Cancer: Short-term exposure to manganese may cause irritation to the eyes, nose, throat, and respiratory tract. Long-term exposure to manganese may affect the central nervous system, causing a psychosis which may include symptoms similar to Parkinson's disease (Sittig, 1991). Respiratory effects may also be seen (U.S. EPA, 1994a).

A chronic non-cancer Reference Exposure Level (REL) of $0.4 \mu\text{g}/\text{m}^3$ is listed for manganese and manganese compounds in the California Air Pollution Control Officers Association Air Toxics “Hot Spots” Program, Revised 1992 Risk Assessment Guidelines. The toxicological endpoints considered for chronic toxicity are the respiratory, central, and peripheral nervous systems (CAPCOA, 1993).

The U.S. EPA has established a Reference Concentration (RfC) of $0.05 \mu\text{g}/\text{m}^3$ for manganese based on impairment of neurobehavioral function in humans. The U.S. EPA estimates that inhalation of this concentration or less, over a lifetime, would not likely result in the occurrence of chronic non-cancer effects. The U.S. EPA has calculated two oral Reference Doses (RfDs) for manganese, one for drinking water and one for food. The RfD for drinking water is 0.005 milligrams per kilogram per day (mg/kg/d) based on central nervous system effects in humans, and the RfD for food is 0.14 mg/kg/d based on the same effects. The U.S. EPA estimates that consumption of these doses or less, over a lifetime, would not likely result in the occurrence of chronic, non-cancer effects (U.S. EPA, 1994a).

Adverse reproductive effects associated with manganese inhalation exposure are impotence and loss of libido in human males. No information is available on adverse developmental effects of manganese in humans (U.S. EPA, 1994a).

Cancer: No studies are available regarding the carcinogenic effects of manganese and manganese compounds in humans or animals. The U.S. EPA has classified manganese in Group D: Not classifiable as to human carcinogenicity (U.S. EPA, 1994a). The International Agency for Research on Cancer has not classified manganese as to its carcinogenicity (IARC, 1987a). Manganese-containing pesticides, mancozeb and maneb, are listed by the State of California under Proposition 65 as carcinogens (CCR, 1996).

